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EDITORIAL

Roads

THE other day going through some family correspondence we came across a letter we wrote in the year 1897 in which we described a ride in a motor-car driven by a friend, a pioneer in motoring, the late Mr. C. S. Rolls. The letter described the skill of the driver and stated that his control of the car was so perfect that even when travelling at the rate of sixteen miles an hour he could stop the car in the space of a few feet. Now we think nothing of sixteen miles an hour and motoring is no longer merely an expensive luxury in which a well-off Cambridge undergraduate can indulge; it is in some countries far and away the most popular method of transport for passengers and goods and is steadily growing in popularity. Motor transport is now certain and reliable: you may go out in your best clothes and alight as clean and beautiful as you were when you started, and you are as sure of reaching your destination at the due time as you are of most things in this world. This great advance is due to better cars, better petrol, and better roads; of these three factors we think, looking back on the early days, that far the most important is the great improvement in the roads. The real advance in adapting the roads to motor traffic has taken place since the war; we do not know even the approximate cost of this in Great Britain but the figure is certainly something enormous and it is singular to find that until a few years ago the construction and maintenance of this expensive road system were carried out with very little scientific guidance. Highway construction has now become an important industry and is an important branch of applied science; Prof. Clements teaches the principles of it at South Kensington and many people are engaged in its study in many countries. Those who are professionally concerned in this science and art have their own organizations, journals, and meetings; an important conference, which we describe in this week's JOURNAL, is to be held beginning on November 13 at the Agricultural Hall in London, at the Public Works, Roads, and Transport Congress and Exhibition. Many learned societies and associations have assisted to organize this congress, amongst them the London Section, the Plastics Group, and the Chemical Engineering Group of the Society of Chemical Industry. These bodies and the Congress Organizing Committee are holding conferences on November 14 when six interesting papers will be read by experts from this country, the United States, and Germany. The occasion is one that will attract a large attendance and we have no doubt that the members of our Society who are specially acquainted with the subject will take this opportunity of assisting in so interesting a development. The chemistry and the engineering of such substances as asphalt and bitumen have already received a good deal of attention and as the scientific study of road-making will continue for a long period so, we have no doubt, there will be found new methods and new substances that will in the future require scientific investigation.

Scottish Chemical Industry

The Scottish National Development Council, which was formed under the auspices of the Convention of Royal Burghs and the Association of County Councils in Scotland, came into being during 1931. Among the large number of prominent men who are office-bearers special mention should be made of the President, Lord Elgin, and the Chairman of Executive, Sir James Lithgow. When the Glasgow Section of the Society of Chemical Industry learned that the Council intended to take steps to conduct surveys of some of the main Scottish industries this Section put forward the suggestion that an *ad hoc* technical committee under the auspices of the Council should be set up to make a survey of the Scottish chemical industry. This suggestion was readily accepted and steps were taken in collaboration with the officers and members of the Section to form a committee of which Prof. G. G. Henderson is chairman, Prof. F. J. Wilson, vice-chairman, and Dr. I. V. Hopper, hon. secretary. A number of well-known members of the Society gave valuable service in the compilation of a report which has just been issued (price 6d. net, from the Scottish National Development Council, 39, Elmbank Crescent, Glasgow). Business men, as well as chemists and many others, will be interested in this publication which, we think, does credit to the Development Council and more especially to our Glasgow Section for sponsoring the project and for the task it so largely shouldered in the production. The ramifications of chemistry being so widespread it would have been wellnigh impossible to have inquired into all the divisions outlined in the "Annual Reports of Applied Chemistry," and so the course was adopted of inquiring into the following: heavy chemicals, leather, bleaching, dyeing and calico-printing, rubber manufactures, paint, oil and varnish, chemical plant and machinery, compressed and liquefied gases, destructive distillation of coal, bone and wood, fermentation products, pharmaceutical products, food colours and flavourings, bichromates, firebricks, sanitary earthenware, glazed bricks, disinfectants, oils, fats, and soap. In all instances the report gives a candid statement of the present position of the industries investigated, and in many instances

the historical treatment given to the subject makes clear the notable advances which have been made in Scottish chemical industry in the past. Some of these pioneering efforts have been maintained and retained, but others have suffered from international competition or have migrated to the south. The reasons given for the retention, the disappearance, or the migration of industries should prove of interest to the general reader and of value to the industrialist. In some of its sections, *e.g.*, those dealing with textiles and rubber manufactures, the report deals at length with the serious competition which has to be met from Japanese goods not only in the home markets but in the Empire overseas, and it urges that action be taken to deal with this matter. One effect of this Asiatic competition is that most countries possessing national industries have set up enormous tariffs to protect themselves against this competition, and in so doing they have automatically excluded British products. Reference is also made to transport costs and to taxation. Shrinkage of business caused by over-taxation expresses itself in a general lack of confidence which holds up enterprise on the part of existing firms and restrains new firms from setting foot in certain areas. The resuscitation of the basic industries would entrain the development of new industries and the combined result would greatly broaden the basis of rating. It is a serious handicap to the Scottish coking industry that the bulk of the Indian pig iron imported into Britain should find its way into Scotland and thus keep local coke ovens idle. The deliberations of the committee on the fermentation industry were completed before the repercussions of American legislation on this Scottish industry could be intelligently anticipated; and so the report is lacking in such tit-bits (whispered in the Highlands and trumpeted on 'Change) that Scotland has been swarming with mysterious whisky agents disguised as gillies or sportsmen. But the sober, far-sighted, and somewhat optimistic statement is made that if one looks to the future, to a time say when the number of products made from ethyl alcohol and from other products obtained by fermentation may be almost as numerous as the progeny of coal tar—and such products, being used for other than potable uses, will not be taxed—then one can visualize a bright future for the fermentation industries. Yes, *say when*; and the sooner the better. We think that members of the Society will find much to interest them in this publication.

Cotton Research

The reports presented at the annual meeting of the British Cotton Industry Research Association, which was held at the Shirley Institute last week, afford ample evidence of the Association's virility and of the keen interest which is being displayed in its work by those who, directly and indirectly, are responsible for its upkeep. It was a happy thought which prompted Lord Rutherford, the chairman of the Advisory Council of the Department of Scientific and Industrial Research, and Sir Frank Smith, the secretary of the Department, to attend the meeting, for not only were they thus enabled to see something of the actual work which is being carried on at Didsbury but to learn at first hand the views of members of the Association whose financial interests are so closely interwoven with the development of the cotton industry in this country. There was a time when the Lancashire textile manufacturer was so prosperous and so self-satisfied that he gave little thought to the morrow. So long as he had what was virtually a monopoly so long was he disinclined, even opposed, either to take the chemist and the physicist into his confidence or to enter into an agreement with his co-manufacturers for the purpose of pooling knowledge. To-day the situation is changed; these barriers to progress have, in large measure, been broken down. The manufacturer of Lancashire cotton goods now realizes that science and industry are interdependent; he knows that they are not two things but rather two sides of the same shield; and the crowning example of this change in outlook is to be found in the use which he makes of the liaison department of the Shirley Institute. As Dr. Pickard remarked, the Association has many evidences that the contacts of the staff of the Institute with the trade are being increasingly welcomed, this feature being due very largely to the policy of the council in instituting the liaison department, a department which facilitates the meeting of the staff of the Institute and the mill managers and enables them "to speak, as it were, the same language." Having negotiated this formidable hurdle, the prime necessity is to weld together into a homogeneous whole the different sections of the industry: to disseminate vertical knowledge about the requirements of one section as against the requirements of another is, states Dr. Pickard, one of the main functions of the Institute; and it is gratifying to learn that this is being accomplished. In extending its activities the Institute has also extended its laboratories, the most notable additions during the past year consisting of premises for carrying out experiments with new blowroom machinery for cleaning cotton and the provision of a fading station for the rapid determination of the action of light on dyed fabrics. Whereas the lamps and illuminants hitherto employed for this purpose have led to erroneous conclusions, it is believed that the fading station installed at the Shirley Institute will simulate sunlight so closely that the behaviour of a given dyed fabric in the laboratory will correspond very closely with its behaviour in, say, tropical countries. Hence, this new work which is being carried out at the Institute will be of inestimable value to the dyer and, incidentally, to the merchant and to the consumer of dyed fabrics, for the loss incurred, both in money and in prestige, at the present time by marketing dyed fabrics which will not withstand sunlight cannot be estimated. In conjunction with closely allied investigations, such as those dealing with the influence of dyestuffs on the tendering of cellulose which have been communicated to this JOURNAL and to the *Journal of the Society of Dyers and Colourists*, the work of the fading station should do something towards re-establishing the textile industry of this country. Although a restoration to the high level reached in 1913 is, perhaps, too much to hope for, we believe, along with Mr. H. P. Greg, the chairman of the council of the Association, that the cotton trade here must come out of the slump better than that of other countries if it continues to give its ungrudging support to the British Cotton Industry Research Association.

The Government Laboratory

It is almost impossible to conceive a wider field of analytical work than that which is dealt with by Sir Robert Robertson and his staff at Clement's Inn Passage and the chemical stations situated at the more important ports. And yet an admirable and interesting summary of the operations carried out during the year 1932-33 is presented in the recently-issued Report of the Government Chemist (H.M.S.O., 1933, 9d. net). When we remember that, in addition to the Board of Customs and Excise—which accounts for a large proportion of the analyses—many Government Departments and other public bodies are served by the Laboratory, we realize to some extent the volume and the variety of work which is undertaken. During the period covered by the Report close on half a million samples were analysed, the number being somewhat smaller than that recorded last year. Although routine analysis is obviously the usual practice, Sir Robert reminds us that many examinations, particularly those required for fiscal purposes, often involve a technique which is not available in the recorded methods of examination of the articles under test; hence, he points out, many of the inquiries submitted involve lengthy search and detailed study of the implications of the technical considerations arising from the inquiries, and it happens not infrequently that the only information on a particular aspect of a subject is available in the records of the Laboratory. That a considerable amount of original investigation is necessary in order to deal with the problems that are presented is indicated in some measure by the papers and reports which members of the staff of the Laboratory communicate from time to time. In addition to papers read at meetings of the staff eleven have appeared in various scientific publications during the year covered by the Report. Although the Laboratory is concerned very largely with analyses for fiscal purposes, it plays an important part in promoting the general welfare of the community. For example, all consignments of tea are examined on importation in order to ensure that no tea which is impure and unfit for human food shall pass into the country. Again, the Laboratory carries out work for the Ministry of Health, and ensures that various Public Health Regulations, such as those dealing with the quality of condensed milk and the addition of preservatives and colouring matters to food, are not being contravened. An account of the examination of samples of sea-water in connexion with a scheme of oceanic research provides very interesting reading. This scheme is being carried out by the Fisheries Department of the Ministry of Agriculture and Fisheries, and by the Fishery Board of Scotland, acting in concert with the International Council for the Exploration of the Sea. The objects of the investigations, states the Report, are to determine the influence upon fish life of the salt concentration and to trace the movements of the water, apart from tidal ebb and flow, from one part to another in the sea. Thus the drift of water from place to place is traced by making periodical measurements of the salinity at definite positions and charting the results, these being published in the *Bulletin Hydrographique*. The value of these data to hydrographers and biologists cannot be over-estimated.

THE CHEMISTRY OF CHLOROPHYLL

By KENNETH F. ARMSTRONG

The name chlorophyll was first given to the green leaf pigment in 1817 by Pelletier and Caventou; the structure of the pigment has engaged the attention of chemists since the time of Berzelius.[1] Stokes,[2] who first introduced the use of the spectroscope for the study of pigments, found that the leaf contained a mixture of two yellow and two green pigments. Sorby,[3] using a hint of Stokes', was able to separate the component pigments by distributing them between immiscible solvents, a method which was later to become very important. The relation of chlorophyll to hæmoglobin was originally suggested by Verdeil,[4] and substantiated by the work of Hoppe-Seyler,[5] who obtained what he called dichromatinic acid, obviously a porphyrin, from an alkali melt, and later by Schunck[6] and by Marchlewski.[7]

Most of these workers used isolation methods which were altogether too drastic, and when Willstätter took up the subject, pure homogeneous chlorophyll preparations had yet to be prepared. At different times phosphorus, iron, sulphur, sodium, and potassium had been incorrectly assumed to be constituents of the molecule, while magnesium had been almost overlooked. The work of R. Willstätter[8] and his collaborators formed the basis for a detailed knowledge of the chemistry of chlorophyll. Chemists are indebted to Willstätter for the methods developed by him for the extraction of the natural pigments in unaltered form from the plant, a problem which much confused the early workers; the difficulties of such extraction are still a source of error. He also introduced the method of "acid fractionation" as a means of purification; it consists in extraction from ether with hydrochloric acid of various strengths. Selective extraction is obtained because small differences in basicity and in solubility result in very different distribution ratios between ether and acid for different substances. The "acid number" of a substance is defined as that percentage concentration of hydrochloric acid which extracts two-thirds of the substance from an equal volume of an ether solution. Operations are controlled throughout by observation of the sharply-banded absorption spectrum of these compounds, which gives an invaluable tool for checking homogeneity and proving identity of material from different sources. The substances form methyl esters of good crystallizing powers which are used for comparison by mixed melting point.

The analytical composition of chlorophyll, as established by Willstätter, stands to-day. He first recognized the part played by magnesium and characterized two ester groups, one esterified with methyl alcohol and the other by phytol. The presence of pyrrole rings was demonstrated by the isolation of pyrroles and of compounds derived from pyrroles in reduction and oxidation experiments. Reduction and oxidation of the blood pigment gave similar results.

A knowledge of the fine structure of chlorophyll only became possible with the elucidation of the structure of

the porphyrins by the elegant methods of synthesis of Hans Fischer.[9]

The time is peculiarly ripe for an objective review of chlorophyll chemistry. A definite formula has been *proposed by Hans Fischer, while alternative structures* have been proposed by J. B. Conant and by A. Stoll. In the following review, for the sake of brevity and clarity, a logical rather than an historical development of structure will be followed. A feature of the field is the unsystematic nomenclature, but usage finds this a preferable alternative to the extremely lengthy systematic names.

Willstätter showed that the two components of the leaf pigment, chlorophyll *a* and chlorophyll *b*, occur throughout higher plants in the proportions of approximately three to one: in certain algæ, however, the *proportion of chlorophyll b becomes vanishingly small.* This observation, together with the known chemical relation of chlorophyll *a* to *b* would seem to exclude the suggestion once made by Willstätter that an equilibrium between chlorophyll *a* and *b* plays any part in the photosynthetic process. Recently, Conant[10] has made it probable that chlorophyll *a* is not homo*geneous, and that varying with the source the main* constituent may be accompanied by an isomeric chlorophyll a_2.

Chlorophyll *a* can be separated from chlorophyll *b* by shaking out the latter with 90% methyl alcohol from a petroleum ether solution of the mixture. It is a bluish-black waxy solid giving a blue-green ether solution, but has never been obtained pure. It gives 4·5% magnesium oxide as ash. In alcohol solution under the influence of the enzyme chlorophyllase, an ester group in chlorophyll is replaced by the solvent alcohol. The products (using ethyl alcohol) are ethyl chlorophyllide and the alcohol phytol. The constitution of phytol, $C_{20}H_{39}OH$, was brilliantly established and proved by synthesis by *Gottwalt Fischer.*[11]

The magnesium can be removed from chlorophyll *a with oxalic acid, forming phæophytin a, still retaining* the phytol. Strong acid hydrolyses the phytyl group forming phæophorbide *a*, which on esterification gives methyl phæophorbide *a*, a dimethoxy compound: phæophorbide *a* itself contains one methoxy group.

The chlorophyllides and phæophorbides can be purified by *recrystallization and accurately analysed,* and the formula for chlorophyll is derived from these; fairly good analyses of the two chlorophylls have recently been obtained.[12]

Saponification of phæophorbide *a* yields phytochlorin *e* (abbreviated to chlorin *e*), a tribasic acid which gives a trimethyl ester. Analogous transformations are undergone by chlorophyll *b*, the compound corresponding to chlorin *e* being known as rhodin *g*. It is customary to prepare the mixed phæophorbides from phæophytin *a* plus *b*, and to separate the *a* and *b* series compounds at this stage by acid fractionation. Chlorin *e* and rhodin *g* can be similarly separated.

The inter-relations of these compounds and their accepted analytical compositions are as follows:

Chlorophyll *a* —Oxalic acid→ **Phæophytin *a***

$C_{55}H_{72}N_4O_5Mg$ ⟶ $C_{55}H_{74}N_4O_5$

$C_{32}H_{30}N_4OMg\begin{cases}COOCH_3\\COOC_{20}H_{39}\end{cases}$ $C_{32}H_{32}N_4O\begin{cases}COOCH_3\\COOC_{20}H_{39}\end{cases}$

↓ Chlorophyllase in ethyl alcohol — ↓ Concentrated HCl

Ethylchlorophyllide *a* — **Phæophorbide *a***

$C_{37}H_{38}N_4O_5Mg$ — $C_{35}H_{36}N_4O_5$

$C_{32}H_{30}N_4O\ Mg\begin{cases}COOCH_3\\COOC_2H_5\end{cases}$ — $C_{32}H_{32}N_4O\begin{cases}COOCH_3\\COOH\end{cases}$

↓ Alkaline saponification

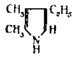
Chlorin *e*

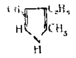
$C_{34}H_{36}N_4O_6$

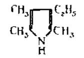
$C_{31}H_{33}N_4\begin{cases}COOH\\COOH\\COOH\end{cases}$

Phæophorbide *a* corresponds in composition to a monomethyl chlorin *e* minus one molecule of water.

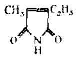
The pyrrole nature of the chlorophyll pigments is established by the products of their reduction and oxidation. Reduction of chlorin *e* or ethyl chlorophyllide yields hæmopyrrole, kryptopyrrole, and phyllopyrrole.

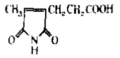

Haemopyrrole


Kryptopyrrole


Phyllopyrrole

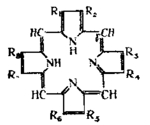
Methylethyl maleinimide and hæmatinic acid are oxidation products.





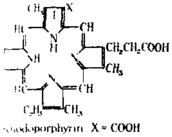
By drastic alkaline degradation of chlorin *e*, according to the conditions employed, a number of porphyrins are obtained.[13]

The products are the dicarboxylic acid verdoporphyrin, which is easily changed into the more stable isomeric rhodoporphyrin $C_{32}H_{34}O_4N_4$ which accompanies it, and the monocarboxylic acids phylloporphyrin $C_{32}H_{36}O_2N_4$ and pyrroporphyrin $C_{31}H_{34}O_2N_4$. More energetic alkali treatment converts both rhodo- and phyllo-porphyrins into pyrroporphyrin, the stable product under these conditions. Fischer has proved that porphyrins have the carbon skeleton first suggested by Kuster;[14] the porphin nucleus has a possibility of eight substituents in the porphyrin. The position of the double bonds is arbitrary, several alternatives being possible.

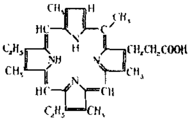


Oxidation of brominated pyrro- and phyllo-porphyrins yields brom-citraconimide,[15] proving that in one

pyrrole ring there is a free β-position. Rhodoporphyrin has this position occupied by a carboxyl group. The constitutions of rhodo-, phyllo-, and pyrro-porphyrins have been unequivocally settled by degradation and synthesis.[16]

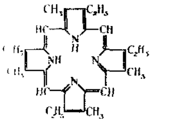


Rhodoporphyrin X = COOH
Pyrroporphyrin X = H

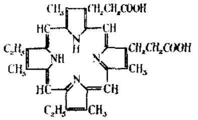


Phylloporphyrin

Under certain conditions the propionic acid groups in pyrro- and phyllo-porphyrins are decarboxylated to ethyl groups yielding respectively pyrro- and phyllo-aetioporphyrins which differ from the aetioporphyrin III obtained from the protoporphyrin of hæmin in having a free β-position. Fischer and Riedl[17] were able to replace the hydrogen of the free β-position in pyrroporphyrin with a propionic acid group, thus synthesizing a product identical with the *mesoporphyrin obtained* from hæmin. A transformation from the chlorophyll to the blood pigment series was thus accomplished.



Aetioporphyrin III

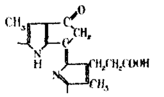


Mesoporphyrin

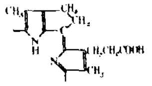
Drastic alkaline degradation establishes the main skeleton of chlorophyll *a*, only two carbons being lost in degrading chlorin *e* to phyllo- or rhodo-porphyrins. The methyl group on the bridge or γ-position in phylloporphyrin indicates the point of attachment of a side-chain.

The porphyrins are, however, different chemically and physically from chlorin *e* and the substances which are more nearly related to chlorophyll. Fischer therefore sought milder methods of degradation. Hydrogen iodide in glacial acetic acids at 50° converts many chlorophyll derivatives into colourless leuco-compounds which re-oxidize in air to porphyrins which retain the full carbon skeleton of the original compound.[18] Phæophorbide *a* with hydrogen iodide gives the isomeric phæoporphyrin a_5,[19] which contains one free carboxyl group, one carbomethoxy group, and one ketone carbonyl. Further treatment with hydrogen iodide eliminates the carbomethoxy group, forming phylloerythrin $C_{33}H_{34}O_3N_4$. Phylloerythrin is also obtained directly from phæophytin, chlorophyllide, and the phæophorbides of the *a* series,[20] by refluxing in 20% hydrochloric acid for 16 hours.

The importance of phylloerythrin lies in that it is also a biological degradation product of chlorophyll. Discovered by Marchlewski[21] in cows' fæces and in the bile of sheep, he rightly claimed it to be a chlorophyll derivative, and showed *it to be identical with the* bilipurpurin found in ox bile by Löbisch and Fischler[22, 23] and with the choleohæmatin of MacMunn. Phylloerythrin is degraded by sodium methylate to give rhodo-, phyllo-, and pyrro-porphyrins. In methyl alcoholic potash in the cold in a stream of air, it is hydrolyzed and oxidized to rhodoporphyrin γ-carboxylic acid. It contains a reactive carbonyl group and can be reduced by the Wolff-Kishner method to desoxophylloerythrin. Desoxophylloerythrin is obtained by the action of hydrobromic acid in acetic acid at 180° on phæophorbide *a*. The proposed formulæ[24] for these compounds contain a carbocylic ring.



Phylloerythrin



Desoxophylloerythrin

(Partial formulæ will be used hereafter)

Desoxophylloerythrin was synthesized by Fischer and Riedmair;[25] on oxidation with oleum containing sulphur, it furnishes phylloerythrin in 10% yield. If methyl phæophorbide *a* is heated in pyridine with sodium carbonate, the carbomethoxy group is eliminated, forming methyl pyrophæophorbide, which is spectroscopically identical with phæophorbide, and yields an oxime. It is isomeric with phylloerythrin and is transformed into it with hydrogen iodide. The production of a biological degradation product of chlorophyll by a laboratory method convinced Fischer of the essential mildness of the hydrogen iodide reagent, and the absence of secondary syntheses, and indicated the existence of the carbocylic ring of phylloerythrin in chlorophyll itself.

Fischer and Hendschel[26] found a number of substances in sheep fæces which are similar to and probably isomeric with pyrophæophorbide, called probophorbides, and evidently represent an intermediate stage in the degradation to phylloerythrin, into which they are transformed by hydrogen iodide. Chlorin *e* also is a biological degradation product, being found in caterpillar fæces. In the stomach of the cow degradation is carried further to phyllo-, rhodo-, and pyrro-porphyrins.[27] It may be noted that Fischer has found that organisms appear to be able to synthesize the carbocylic ring from open chain compounds, thus *Penicillium* and *Aspergillus* converted chlorin *e* into a porphyrin probably identical with phylloerythrin.[28]

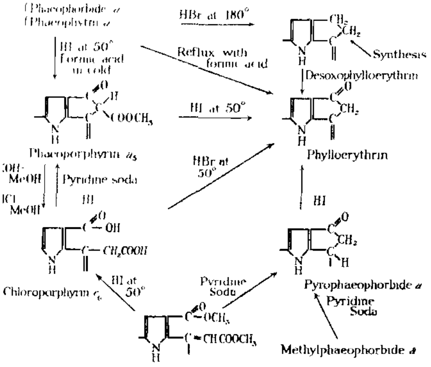
Chlorin *e* is best represented as a modified rhodoporphyrin skeleton bearing the group —CH(OH)COOH in the γ-position; on oxidation with potassium molybdicyanide[29] it loses carbon dioxide forming chlorin *k*.* The analyses of both chlorin *e* and its trimethylester correspond to an anhydrous formula,[30] but the free acid is hygroscopic, readily adding a molecule of water

* The term chlorin is applied to a large class of chlorophyll *a* derivatives, characterized by a green ether solution and very similar absorption spectrum. They are less basic than those porphyrins which contain an identically substituted porphin skeleton.

giving the hydroxy acid. The trimethyl ester presumably contains the side chain : γ C = CH COOCH$_3$;[31] on heating in pyridine-soda, it is converted in 10% yield into methyl pyrophæophorbide *a*.[32]

Chlorin *e* trimethyl ester is converted by hydrogen iodide into chloroporphyrin e_6, to which is assigned the structure of rhodoporphyrin γ-acetic acid. Chloroporphyrin e_6 is converted by pyridine-soda, or by hydrogen iodide in acetic acid, into phæoporphyrin a_5, a ring synthesis. The transformation is reversed with hydrogen chloride or with methyl alcoholic potash in the cold. Hydrogen bromide converts it into phylloerythrin. Hydrogen iodide can effect a ring synthesis as well as convert chlorophyll derivatives into porphyrins.

These transformations (as viewed by Fischer) are expressed in the scheme :



For further progress it is necessary to consider the phenomena of the " allomerization " and " phase test " of chlorophyll. Chlorophyll is extremely sensitive to oxidizing agents and to air. Willstätter and Utzinger[33] characterized as allomerization the process which occurs when chlorophyll stands in alcohol solution. It was found by Conant, Kamerling, and Steele,[34] using a modified Warburg apparatus, that two equivalents of oxygen are absorbed in allomerization ; alternatively two equivalents of potassium molybdicyanide are used. The process is therefore a dehydrogenation. The product obtained from methyl phæophorbide, dehydro methyl phæophorbide, is spectroscopically almost identical with the starting material but differs in that it gives no chlorin *e* on saponification.

The " phase test " is a colour reaction given by chlorophyll derivatives on shaking their ether solutions with strong methyl alcoholic potash. Unallomerized chlorophyllide *a*, phæophorbide *a*, and chlorin *e* trimethyl ester give a bright yellow-brown colour which in a few seconds gives place to green. In the *b* ser the transitory phase colour is reddish brown. Duri the phase test oxygen is absorbed[35] and hydroly occurs and the products are the same unstable chlori which result from the hydrolysis of dehydro metl phæophorbide. The initial process in the phase test therefore a dehydrogenation (allomerization), which followed by hydrolysis. The essential process is oxidative hydrolysis.

A similar interpretation of allomerization as initia a dehydrogenation is given by Fischer. In the all merization of chlorophyllide in ethyl alcohol wi *quinone as hydrogen acceptor, one mole of hydroquin* is formed.[36]

The structure of chlorophyll and allomerized chlo phyll has been elucidated by Fischer from a study of t action of hydrogen iodide on these substances.

Native phæophytin, or the derived methyl phæoph bide *a*, obtained from leaves by the Willstätter p cedure, gives with hydrogen iodide phæoporphyrin If methyl phæophorbide *a* is allomerized by the acti of oxygen or iodine in acetic acid, and the produ treated with hydrogen iodide, phæoporphyrin a_7, which is assigned the structure of rhodoporphy γ-glyoxalic acid, is obtained. The analysis of al merized methyl phæophorbide corresponds $C_{36}H_{38}N_4O_6$, while that of methyl phæophorbi corresponds to $C_{36}H_{38}N_4O_5$. Fischer[37] therefo interprets allomerization as due to a dehydrogenati followed by addition of a molecule of water, giving ox methylphæophorbide *a*. Similarly chlorophyllide c be allomerized with quinone or oxygen in alcohol, whe upon hydrogen iodide yields phæoporphyrin a_6 : c hydrogenation is followed by addition of alcohol to t *double bond. With oxygen in acetic acid* chlo phyllide is allomerized and the product of hydrog iodide degradation is *nor*-phæoporphyrin a_6, in whi water instead of alcohol has added to the double bon Chlorophyllide is allomerized in alcohol with oxyge but phæophorbide is stable under these conditio and can only be allomerized in acid. The magnesiu evidently has an activating effect. These transform tions are interpreted as shown in the next column.

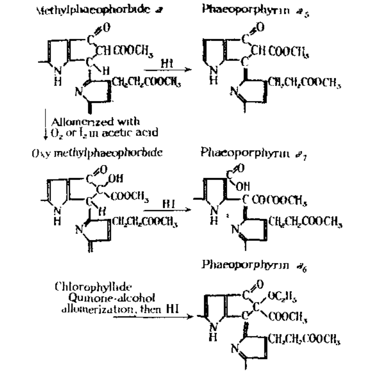
Methyl phæophorbide forms an oxime,[38] but only wi some difficulty on heating, whereby secondary chang are not excluded.

The position of the phytol in chlorophyll was fi correctly placed by Conant.[39] Chlorophyll *a* by lo of phytol and magnesium yields phæophorbide *a* wi one free acid group. On pyrolysis this loses a carb methoxy group forming pyro-phæophorbide *a*, whi has a free acid group.[40] This must be the propion acid group to survive pyrolysis and the phytol must l attached to the propionic acid group.

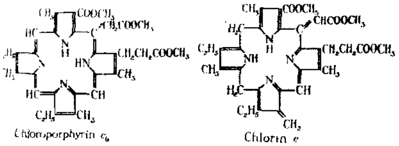
Fischer was first in error[41] as to the position of t phytol, but subsequently placed it correctly.[42] Eth chlorophyllide in which the ethyl group replac the phytol, yields with hydrogen iodide the ethyl est

*** The term unstable is used because in contrast to norm chlorins, these chlorins on treatment with diazomethane, or standing some time in ether solution, are converted into su stances with an entirely different colour and absorption spectru known as purpurins.**

... phæoporphyrin a_5 which, on heating over a free flame, is converted into phylloerythrin ethyl ester. The ... and therefore the phytyl group must be on the propionic side chain, and the carbomethoxy group be attached to the carbocylic ring.

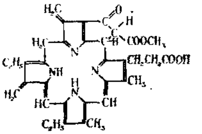


The fine structure of Fischer's chlorophyll *a* formula can now be discussed. Chlorophyll and the chlorins are regarded as derived from an *iso*porphyrin ring. Thus chlorin *e* is isomeric with chloroporphyrin e_6, and this is expressed as follows, the distribution of double bonds being admittedly arbitrary.[43]



Chloroporphyrin e_6 Chlorin *e*

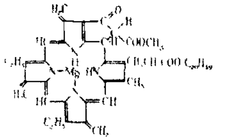
In a similar way phæoporphyrin a_5 and the isomeric phæophorbide *a* are related. Phæophorbide *a* contains the *iso*porphyrin ring and in addition contains two readily removed hydrogens. Fischer, in order to accommodate these requirements with the analyses, extracts two hydrogens from the nucleus forming two methylene groups. Phæophorbide *a* is given the structure :[44]



Phaeophorbide *a*

Combustion analysis alone cannot distinguish from a formula richer by two hydrogens, but Fischer quotes unpublished data on heats of combustion in support of the isomerism with phæoporphyrin a_5. The transient yellow phase in the phase test is attributed to a potassium salt of the enol form of the keto group.[45]

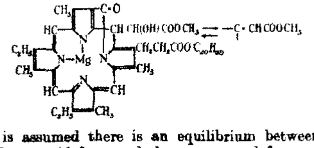
For chlorophyll itself still further modification of the *iso*porphyrin nucleus is deemed necessary :



Zerewitinoff determinations with the chlorophyllides indicate two active hydrogens, hence these are placed on the two pyrrole rings which are unoccupied in binding the magnesium, and the conjugated system is rearranged accordingly. Fischer cites as support for this the fact that chlorophyll has a different type of spectrum from other phyllins (magnesium derivatives) which have been prepared. The way in which the magnesium is bound is by no means clear. The porphyrin ring has all the pyrrole rings in the same plane and the same holds in all probability for chlorophyll derivatives. Magnesium in its 4-covalent complexes has a tetrahedral structure which seems to preclude the two remaining nitrogens from being coordinated with the metal. The above formulation gives a fairly consistent interpretation of Fischer's own results, but is not necessarily a unique interpretation.

No chemical evidence exists for the methylene groups either in the chlorophyllides or the phæophorbides and it would seem unwise to rely on the Zerewitinoff determinations which give for the most part inconsistent and uninterpretable results in the chlorophyll and porphyrin series.[46] The similarity in spectra of phæophorbide and chlorin *e* speaks against their possessing different conjugated systems. The formula explains only with difficulty the formation of chlorin *e* on hydrolysis of phæophorbide : it must be assumed that the substance with a γ-acetic acid side chain first formed, undergoes isomeric change to the unsaturated side chain structure of chlorin *e*.

Conant regards chlorophyll *a* as equivalent to monomethyl chlorin *e* minus one molecule of water. Fischer's formula is regarded as inadequate to express the formation of chlorin *e* from phæophorbide, nor is it regarded as proved that there exists a carbocylic ring in chlorophyll. An open chain formula containing a lactam group is preferred :



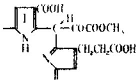
It is assumed there is an equilibrium between the α-hydroxy acid form and the unsaturated form as was postulated by Conant and Armstrong[47] for the esters

of chlorin *e*. The formula is in agreement with the analyses with the yielding of chlorin *e* on hydrolysis, and the secondary alcohol group is the seat of the dehydrogenation in allomerization and phase test. If this formula be true, the structures containing carbocylic rings for the porphyrins phylloerythrin and phæoporphyrin a_5, proposed by Fischer, are still acceptable, but it must be assumed that these porphyrins are synthesized in the hydrogen iodide reaction from the open chain compounds. Fischer himself has shown that hydrogen iodide converts chloroporphyrin e_6 into phæoporpbyrin a_5.[48]

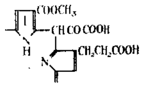
The lactam formula raises certain serious stereochemical difficulties, an answer to which must wait on greater knowledge of the orientation of the pyrrole rings in the molecule. It would appear that the lactam ring must be considerably strained.

The methods of degradation which have been used by Conant throw considerable light on the nature of the tetrapyrrole nucleus in chlorophyll series. When methyl phæophorbide *a* is submitted to mild conditions of oxidative hydrolysis, the product is the unstable chlorin, monomethyl chlorin *g*.[49]

To this is assigned the structure of the keto acid analogue of chlorin *e*: carbonyl reagents do not react, so an enolized form may be stabilized.



Monomethyl chlorin *g*



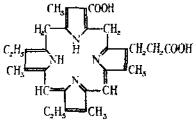
Phæopurpurin 7

Monomethyl chlorin *g* is converted by diazomethane into a product of entirely different colour known as dimethyl phæopurpurin 7. Phæopurpurin 7, which is a monomethyl ester, is obtained on saponification with alcoholic potash. It is isomeric with monomethyl chlorin *g* and contains a carbomethoxy group on ring I instead of on the bridge.

Saponification with boiling alkali eliminates oxalic acid from phæopurpurin 7, forming a new dibasic substance chlorin *f*, $C_{32}H_{36}O_4N_4$. Pyrolysis of phæopurpurin 7 in boiling diphenyl yields a monomethyl chlorin *f* together with carbon dioxide and carbon monoxide.

The substance chlorin *f* is important, since it is a simple chlorin derived from chlorophyll by such transformations as would not alter the state of oxidation of the nucleus. The hydrogen iodide reagent on the other hand alters completely the condition of the nucleus. Chlorin *f* appears from the analyses definitely to contain two more hydrogens than the corresponding porphyrin rhodoporphyrin.[50] It is converted by hydrogen iodide into rhodoporphyrin; this process involves reduction and reoxidation of a leuco compound. Dehydrogenation of chlorin *f* with molybdicyanide requires two equivalents of the reagent and converts it into *iso*rhodoporphyrin: the same change is brought about by the action of air on the hot alkaline solution of a metal derivative of chlorin *f*. *Iso*rhodoporpbyrin is also produced by the pyrolysis of monomethyl chlorin *g*. *Iso*rhodoporphyrin appears to be identical with the *pseudo*-verdoporphyrin of Fischer,[51] and it is isomeric with rhodoporphyrin and is converted into the la... by hydrogen iodide or by treatment with strong alkali at 190°. Chlorin *f* is regarded by Conant as a dihydro *iso*rhodoporhphyrin.

The Conant formulation of chlorins (being two hydro gens richer) avoids the assumption of Fischer that meth... ene groups are present. Chlorin *e* is represented a chlorin *f* γ-glycolic acid minus water and is therefor still isomeric with chloroporphyrin e_6 as Fischer contends phæophorbide *a* would be regarded as richer by tw hydrogens than phæoporphyrin a_5. Fischer cites hea of combustion data in support of his analyses. Benzen and dihydrobenzene have almost identical heats of com bustion, and *iso*rhodoporphyrin and chlorin *f* bear according to Conant, the same relation to each othe and would probably be indistinguishable by therm chemical data.



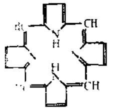
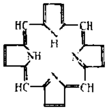
Chlorin *f*

The results suggest that chlorophyll and the chlori are more closely related to the *iso*porphyrins than t the true porphyrins. Treibs and Wiedemann[52] e pressed a similar opinion on verdoporphyrin (a thi isomer of rhodoporphyrin). The nature of verd porphyrin requires reinvestigation. The formulation the chlorins as dihydroporphyrins is supported b measurements of absorption spectra at low temperatur by Conant and Kamerling,[53] which showed striking pa allels between benzene and dihydrobenzene on the o hand and porphyrins and chlorins on the other. A lar number of ways of writing a dihydroporphyrin a possible, but at present there are few methods for di criminating between them. This is an importa problem in which aid from physical methods will ha to be invoked. It would also be valuable to establi relations between the colour of these compounds and t type of conjugated system as was done by Kuhn for t polyene pigments. It might then be possible to diffe entiate between the various chlorophyll formulæ pr posed, which have very different types of conjugat system.

Several types of chlorin are known, the norm chlorins, the unstable chlorins, which change over in purpurins, and the synthetic chlorins of Fischer,[54] whi on reoxidation after reduction with sodium amalga are regenerated, whereas normal chlorins yield po phyrins on oxidation following reduction.

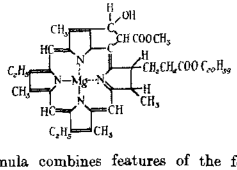
The nature of the isomerism between rhodoporphyr and *iso*rhodoporphyrin and perhaps also verdoporphyr remains unexplained. It is possible to write two po phyrin formulæ in which the hydrogen born by t nitrogens are on *cis* and *trans* pyrrole rings respectivel Several alternative ways of writing the double bonds a possible, but in the course of Fischer's porphyrin sy theses, it was never possible to produce isomers whi it was necessary to account for in this way.

... introduction of formulæ containing free radicals, as ... been done by Clar and Haurowitz[55] seems ground-l... and unnecessary in the present state of knowledge.

Conant and Bailey failed to interconvert rhodo- and ... rhodoporphyrins by regeneration from their zinc complex salts, as might be expected from the above two formulæ whose metal derivatives would be electronic isomers. Treibs and Wiedemann regenerated verdo-porphyrin from its magnesium complex.[56] It may be ...ary to remark here that although Fischer's syntheses ... natural porphyrins and, in several instances, of all the predicted isomers of a given porphyrin make the truth of the porphyrin structure established almost beyond question, the methods of synthesis by their nature do not prove the structure. It is desirable that a synthesis which affords a positive proof of structure should be devised.

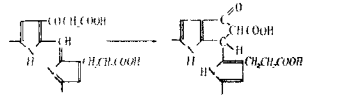
A number of contributions to the chemistry of chlorophyll have been recently made by A. Stoll,[57] whose work with Willstätter on its chemistry and photosynthetic role is well known. With the exception of the three last, all these papers have been theoretical, and a detailed discussion of them must be deferred until the full experimental results are published: it is profitable at this time to make certain criticisms of the formula for chlorophyll which he has proposed:



The formula combines features of the formulæ of Conant and Fischer and has peculiarities of its own. Allomerization is explained by dehydrogenation of the secondary alcohol group, the transformations with hydrogen iodide are interpreted as by Fischer. The formula is four hydrogens richer than that of Fischer. The conjugated system is the same length as in a porphyrin, with one pyrrole ring bearing two additional hydrogens; like Conant's formula, it possesses a dihydroporphyrin nucleus. As experimental support[58] here is cited, the non-formation of an oxime by phæophorbide, and the formation of an oxime by allomerized phæophorbide. A benzoyl derivative which is very easily hydrolyzed and gives the phase test, with hydrolysis of the benzoyl group, is given by phæophorbide, and also appears by derivatives of allomerized chlorophyll.

The formula does not explain the formation of chlorin by saponification of unallomerized chlorophyll derivatives, a property insisted on by Willstätter, and since then many times confirmed by Fischer and by Conant. Chlorin *e* is produced even in presence of reducing agents.[59] If Stoll's formula is correct the substance produced instead of chlorin *e* would have a free aldehyde group, which has not so far been observed.

The structure of chlorophyll *b* is far less certain than that of chlorophyll *a*. The transformations parallel those in the *a* series but in all cases yields are poorer and the products more difficult to obtain pure. Chlorophyll *b* contains two hydrogens less and one oxygen more than chlorophyll *a*, and contains in fact a reactive carbonyl group which persists throughout the compounds of the *b* series. The three groups of workers all differ in the position which they consider the carbonyl group to occupy. Fischer[60] places it in the propionic acid side chain, as a β-*keto acid*; *Conant and Dietz*[61] replace by C = O the CH_2 group on the bridge between the pyrrole rings; Stoll and Wiedemann[62] place the carbonyl group in the side chain on the γ-bridge as an α-keto acid. It is hardly profitable in the present state of controversy to discuss the respective merits of these formulæ, to all of which objections can be raised. It should be pointed out that if Conant's formula for chlorophyll *a* be true, the structural relation between the porphyrin components of chlorophyll and hæmin is lessened, the carbon skeleton of propionic acid in the latter having migrated to the carbon bridge in the former. The migration is certainly a fact in chlorin *e* and phylloporphyrin, both degradation products in nature. It is a tempting speculation to imagine the formation of chlorophyll *a* from a precursor of the same carbon skeleton as mesoporphyrin, possessing a β-keto acid side chain (the precursor of chlorophyll *b* would possess two such side chains if Fischer's formula be true) by addition at the bridge carbon to the porphin nucleus.



It seems to me that a satisfactory formula for chlorophyll *a* will have to include the views of Conant on the structure of the nucleus which are better substantiated than those of Fischer, together with the carbocylic ring of Fischer. Before this can be advanced, it will be necessary to reinvestigate the question of whether chlorin *e* can be produced from chlorophyll and the phæophorbides without the preliminary dehydrogenation contended to be necessary by Stoll.

Stoll and Wiedemann[63] were able to overcome the technical difficulties and show that both chlorophyll *a* and chlorophyll *b* are optically active. Chlorophyll *a* and *b* have $[\alpha]^{25°}_{7200Å} - 260° \pm 25°$: the magnesium free methyl and phytyl phæophorbides are also optically active.

It is interesting to note that the catalyst which intervenes in the plant's first synthetic act is itself asymmetric, but the discovery throws no light on the problem of whence the asymmetry in vital syntheses springs. The chemical aspects of photosynthesis have been reviewed in another place by Spoehr[64] and it is unnecessary to

deal in detail with them here. The easy dehydrogenation of chlorophyll has led to the suggestion that a reversible reaction

chlorophyll ⇌ dehydrochlorophyll + 2H

supplies the hydrogen for the photochemical reduction of carbon dioxide. Schemes on this basis have been proposed by Conant[65] and also by Stoll.[66] Willstätter[67] has given an interpretation in terms of the radical theory due to him and Haber. All these suggestions are at present pure speculation, though they may provide fruitful hypotheses for experimental work.

There has been interesting work by Emerson[68] and by Emerson and Arnold,[69] who have used very successfully the flashing light method of Warburg on the green alga *Chlorella*. Emerson's early experiments seemed to show a proportionality between the amount of photosynthesis and the chlorophyll content of a culture, thus proving for the first time that chlorophyll intervenes chemically in photosynthesis, and not only as a photosensitizer. Later experiments, however, show a much poorer correlation.[70] Photosynthetic efficiency for a given amount of light energy is enormously increased in intermittent light, and by an ingenious method the rates and the order of the light and dark (Blackman) reaction and other information are obtained, for which reference must be made to the original papers. It is not possible, however, to state which molecular species is involved in these reactions, nor whether, nor in what form, chlorophyll intervenes chemically. It has not yet been possible, therefore, to apply the advances in the knowledge of the chemical structure of chlorophyll to a solution of the photosynthesis problem.

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NOTE ON THE TAFFEL AND REVIS METHOD FOR ESTIMATING THE RANCIDITY OF OILS AND FATS

By J. K. GILES

Taffel and Revis describe (J.S.C.I. **50**, 89 T) separate methods for estimating the rancidity of fats that have become rancid at high and moderate temperatures. This note refers only to their methods for fats that have become rancid at moderate temperatures. Method 1(*a*) which is carried out in the cold is obviously unsuitable for solid fats. Method 1(*b*) is as follows:

10 g. of the oil, 40 c.c. of glacial acetic acid, and either 2 g. of barium iodide or 2 c.c. of 50% potassium iodide solution are put into a strong 60-c.c. bottle provided with a well-fitting glass stopper. The air remaining in the bottle is displaced with carbon dioxide, and, after

...erting the stopper, the bottle is carefully placed in boiling water and left there for two minutes. It is then removed and shaken for 2 minutes, and a cloth wrapped round it, then replaced in the boiling water for 2 minutes, and is finally again removed and shaken for 2 minutes. Without cooling, the contents of the bottle are poured into 150 c.c. of cold water, a few drops of starch solution are added and the whole is titrated with thiosulphate. A blank is carried out without oil.

In examining fats of very slight rancidity the variability of this blank was found to limit the application of the test. To eliminate atmospheric oxygen more thoroughly from the reaction bottle a current of CO_2 was passed through the hot glacial acetic acid before adding the potassium iodide and fat, and continued until the action was complete. In this way blanks of 0·2 ml. of 0·02N-thiosulphate were obtained. In addition to preventing atmospheric oxidation the current of CO_2 keeps the fat emulsified with the acetic acid and saves the necessity for the alternate heating and shaking in the above method. The modified test is as follows:

Pour about 11 ml. of the melted fat into a 10-ml. measuring cylinder. Counterpoise on a balance to 0·05 gm. and keep warm. Take 40 ml. of glacial acetic acid in a 2-oz. bottle and clamp up to the neck in water at 95° to 100° C. Pass through a steady stream of CO_2 from the Kipp's apparatus by a glass tube drawn to a fairly fine capillary and resting loosely in the bottle. When the CO_2 has been passing for 2 minutes run in 2 ml. of 50% potassium iodide without stopping the CO_2. Not more than a very slight tint of yellow should appear. After a further minute pour in the liquid fat and find the weight added by reweighing the cylinder. On the addition of the fat iodine is rapidly set free. Continue passing CO_2 for a further 4 minutes. Remove bottle and tube from water bath. Pour the contents into 150 ml. of distilled water in an 8-oz. W.M. stoppered bottle, rinsing small bottle and tube. Add starch solution and titrate with N/50 thiosulphate. (The final colouring is not blue but yellow or grey. The end point is reached when 2 drops of thiosulphate fail to give a distinct brightening colour). Carry out a blank.

It might be expected that some loss of iodine would occur by volatilization. This was tested for as follows:

		ml. 0·02N-thiosulphate
1. *Blank*		
35 ml. acetic acid 5 ml. sol. of I in acetic acid 2 ml. 50% KI solution	titrated cold	3·25
2. *Oxidation of KI at* 95°—100° *C.*		
35 ml. acetic acid—CO_2 passed 2 min. 5 ml. acetic acid 2 ml. 50% KI sol.	added and CO_2 passed	0·22
3. *Oxidation and volatilization at* 95°—100° *C.*		
35 ml. acetic acid—CO_2 passed 2 min. 5 ml. sol. of I in acetic acid 2 ml. 50% KI sol.	added and CO_2 passed further 5 min.	3·44
4. *Oxidation and volatilization at* 95°—100° *C.*		
As (3) but CO_2 passed for a further 10 min.		3·45

Hence volatilization by difference is 0·03 ml. and 0·02 ml. for experiments 3 and 4 respectively. This is within the error of experiment, and no increase is shown by 4 over 3.

In the author's experience this modification makes the Taffel and Revis test more convenient and more accurate, especially for fats of very slight rancidity. The author is indebted to Messrs. Gray Dunn & Co., for permission to publish this note of work done in their laboratory.

PRESENTATION TO SIR CHRISTOPHER CLAYTON

At the annual luncheon of the Widnes Chamber of Commerce on October 3 Sir George Christopher Clayton, M.P., was presented with an illuminated address congratulating him on the knighthood conferred upon him this year. Sir Christopher is the president of the Institute of Chemistry and a director of Imperial Chemical Industries, Ltd., and speakers at the luncheon paid tribute to the important part played by him in the development of chemical industry in this country, particularly in Widnes.

Sir Max Muspratt, who presided at the luncheon, said that "three musketeers" had come to Widnes at the end of the last century. They were the late Mr. Arthur Carey, Sir Christopher, and himself, and Sir Max was convinced that Sir Christopher was the most able of the three. Between them they had had a great reponsibility in reorganizing the processes of the old United Alkali Co., and they were not unsuccessful in carrying them out. When the war came the new processes became second to none, as they had been supreme in old processes. Unfortunately Widnes was not suited to some of the new processes, and in a changing world conditions had become so altered that it had become necessary to face them in an entirely new spirit. Sir Christopher and himself had however looked at such questions from every aspect, not the least being the problems of manual labour and working conditions. Sympathy with these conditions had led them both to take an active part in politics, and Sir Christopher now occupied an important place in the House of Commons. Sir Max referred to the transition from the United Alkali Co. to Imperial Chemical Industries, Ltd., of which both were now loyal members, and said that Widnes would not be neglected, for they knew what Widnes could give to the chemical industry of this country.

The presentation was made by Mr. A. E. Calvert, who said that Sir Christopher was esteemed as a scholar, a scientist, a commercial magnate, and a lover of sport. In replying Sir Christopher said that Sir Max Muspratt had always been his leader, and he was proud to have had his companionship. Together they had been able to do much for Widnes that could not have been done separately. He recalled the difficult task they had had to induce the directors to change from the old Leblanc process to more modern methods. Under the new régime of I.C.I. they were pulling their weight, and everyone was looking forward to future developments. There were many friends of Widnes in London, and future developments would show that Widnes was a very valuable asset. It had now certain advantages that it had not possessed before, and was assured of a successful future.

SOCIETY OF CHEMICAL INDUSTRY

OFFICIAL NOTICES

Public Works, Roads, and Transport Congress and Exhibition (1933), Royal Agricultural Hall, London, N., Nov. 13–18. By arrangement with the County Councils Association a conference will be held on Tuesday, Nov. 14, at the Royal Agricultural Hall, London, N., under the auspices of the Society of Chemical Industry on "The Mechanical Testing of Road Materials." The sessions will commence at 11 a.m. (chairman, Major F. C. Cook, D.S.O., M.C., M.Inst.C.E., Deputy Chief Engineer, Ministry of Transport), and at 3 p.m. (chairman, Prof. G. T. Morgan, O.B.E., D.Sc., F.R.S., Director, Chemical Research Laboratory, Department of Scientific and Industrial Research and past-president of the Society). There will be an informal lunch at 1.30 p.m., when the chair will be taken by Dr. J. T. Dunn, F.I.C., president of the Society.

The conference or symposium has as its object bringing to a focus the scattered scientific knowledge on this subject, of drawing the attention of surveyors, and of engineers, chemists, and physicists to the main lines of research under development in British and foreign laboratories and of obtaining from surveyors and technologists views which will serve as a guide for future work. It is of vital importance that laboratory work be correlated with road results, so that eventually the laboratory figures may be a real guide to the essential properties of a road, namely, durability, stability, safe-riding surface, and economic cost of construction.

Amongst the papers to be read will be the following: "*Laboratory Tests and their Correlation with Full-scale* Road Experiments," by Mr. R. G. C. Batson; "Some Factors Involved in the Mechanical Testing of Bituminous Mixtures," by Mr. W. G. Adam and Mr. D. G. Murdoch; "The Mechanical Testing of Bituminous Road Mixtures," by Mr. Prevost Hubbard; "The Mechanical Testing of Asphalt," by Mr. D. M. Wilson; "Mechanical Tests and the Modern Highway," by Mr. D. C. Broome and Mr. A. R. Thomas; and "Mechanical Testing of Bituminous Road Materials," by Prof. Dr.-Ing. E. Neumann.

The authors will not read their papers but will open the discussion. Copies of the papers will be available shortly, application for which should be made to Mr. F. M. Potter, Hon. Conference Secretary, 46, Finsbury Square, London, E.C.2.

A limited number of complimentary tickets of admission to the exhibition and congress will be available, and application for these should be made to the General Secretary of the Society.

Plastics Exhibition. We announced in a recent number the extension of the Exhibition in response to an appeal from the public and the Trade Association, which was supported by the Plastics Group of this Society. The authorities have now fixed the closing date as January 15, 1934.

GLASGOW SECTION

The first meeting of the Glasgow Section was held jointly with the Institute of Chemistry in the Royal Technical College on Friday, October 6, with Prof. F. J. Wilson in the chair. Dr. J. W. Donaldson, assisted by Mr. D. R. Hutchison, gave a paper on "*Friction Tests on Lubricating Oils.*"

Dr. Donaldson said that in studying lubrication, two distinct types became apparent, fluid film lubrication in which the internal friction of the oil itself played an important part, and partial or boundary lubrication between two metallic surfaces in contact with one another. He proposed to consider the latter. It had been found that under conditions of boundary lubrication oils of similar viscosity produced different results and for want of a better term distinction could only be made by saying that one oil was "oilier" than another: other things being equal the user of a lubricating oil seemed justified in seeking a measure of this "oiliness." Dr. Donaldson described the evolution of a simple mechanical device which gives discriminating results with oils of comparative specifications. The apparatus finally adopted consisted of a ½-in. ball attached to a pendulum and pointer and resting on three ½-in. balls immersed in an oil bath. The smaller ball thus made contact with the larger balls at three points, and by observing the swing of the pendulum as recorded by the pointer it was possible to calculate the coefficient of friction. Dr. Donaldson explained the results which he had obtained from this and earlier apparatus. With mineral oils the coefficient of friction rose with temperature, but with animal and vegetable oils the frictional coefficient rose to a maximum with rise of temperature and then decreased. In concluding Dr. Donaldson said that "oiliness" was only one property of an oil and, important as it was, it had to be considered in relation to other properties before any consideration as to the suitability of an oil for a specific action could be reached. The paper will appear in due course in the Transactions of the JOURNAL.

A discussion was then opened by Mr. Loveless, who commented on the method adopted for measuring the temperature of the oil under test. Since it was the temperature of the bearing seat which was observed he considered that, owing to heat conduction from the ball to the pendulum, the actual temperature of the oil would be lower than that recorded. With regard to the suggestion that the difference in behaviour of mineral oils and animal and vegetable oils might be attributed to absorption effects he said that it seemed to him to depend rather on what might be called the absorption potential, or the tendency of the oil to seep into the bearing owing to capillarity. This would depend largely on surface tension and the decrease in frictional resistance of vegetable oils with increase of temperature should be due to increase in absorption. In this case however it should decrease with rise of temperature. He suggested that the nature of the curves obtained by plotting coefficient of friction against temperature could perhaps be explained as a viscosity effect. Rise of temperature would decrease the viscosity and thus bring the metallic surfaces closer together. Above a certain temperature however further rise would have no effect in bringing the surfaces any closer together.

Mr. MacArthur asked what proportion of fatty oils was included in the compounded oils tested.

..r. Moore suggested that the difference in behaviour ..n by fatty oils might be due to the orientation of .. molecules. Dr. Hopper asked if the apparatus ..ribed was readily available and if its cost was ..ciently low to make its installation in engineering ..ratories feasible.

Mr. Andrew said that with the present methods of ..esting it was impossible to differentiate between .. costing 1s. or 4s. per gal. Oils were now being ..leverly compounded to pass routine tests that engine ..formance became the only criterion. He wondered .. would be possible by means of the apparatus ..ribed to differentiate between a good and a bad

Mr. McKillop pointed out that maximum temperature ..d in testing (250° F.) was lower than that obtaining .. actual practice. The question of "oiliness" was ..portant and evaporation at higher temperatures was ..e of the difficulties with which an engineer had to ..ontend.

Mr. MacCallum thanked Dr. Donaldson for bringing forward a new method of testing oil. He had had some experience of the Thurston oil tester and had found it to be of great assistance.

Replying to the questions raised Mr. D. R. Hutchison said that as to the value of the tests, the results obtained were strictly comparative since the temperature was always taken in the same way. The actual oil temperature did not differ from the temperature of the seat by more than 10° F. With regard to absorption at higher temperatures it was probably true to say that this absorption became less with rise of temperature but it was not true to attribute the superior qualities of vegetable oils to a viscosity effect. In the tests which had been carried out they had arranged to use oils with practically the same viscosities. If, as suggested, pumping occurred then the condition of fluid film lubrication would be established and this could happen without the oil passing under the ball. If fluid film conditions were established the coefficients of friction would not be so high as those determined. He agreed that the orientation of the molecules in fatty oils might offer an explanation of their behaviour. In the compounded oils which they had used there was probably about 5% of fatty oils and compounded oils made by the addition of oleic acid to a mineral oil usually contained about 1% of this acid. It had been found from extensive tests that the addition of more than about ..% fatty oil did not greatly affect the frictional properties. The exact cost of the apparatus had not been quoted, but he thought that it would be about £5. If all the other tests conducted on two different samples of oil agreed and if the test of "oiliness" differed, then he would have no hesitation in using the oil with the superior "oiliness." Mr. Hutchison said that he had used a Thurston oil tester but had found that the results which it gave were erratic. A vote of thanks was accorded to the authors on the proposition of Dr. T. Ewan.

MANCHESTER SECTION

The first meeting of the session was held at the Engineers' Club, Manchester, on October 6, when the new chairman of the Section, Dr. A. Schedler, delivered an address on "Chemistry, Old and New," Dr. T. Callan, M.Sc., presiding.

In his address Dr. Schedler traced the development of chemistry from the mythological ages to recent times, the interesting story being greatly appreciated by a well-attended meeting.

SOCIETY OF PUBLIC ANALYSTS

An ordinary meeting of the Society of Public Analysts was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 4, the president, Mr. F. W. F. Arnaud, in the chair.

Certificates were read in favour of H. G. Coles, A. F. Colson, C. A. Dunbar-Mitchell, A. D. Husband, G. V. James, J. B. McKean, J. G. Peirce, J. Rae, V. Venkatachalam, and A. M. Ward.

The following were elected members of the Society: L. H. James and A. Jones.

The following papers were read and discussed:

"The Occurrence and Origin of Lead in Canned Sardines," by L. H. Lampitt and H. S. Rooke.—Canned sardines have been found to be seriously contaminated with lead. Investigation of the origin of the lead has shown an apparent connexion between the amount of solder exposed in the can and the lead-content of the sardines; solder evidently causes some contamination with lead. But this is not the only source, for sardines packed in cans where no lead could be derived from the container have also shown contamination with lead. It has been proved that sardines cooked on grills covered with so-called "tin" containing appreciable quantities of lead are badly contaminated with this metal, whereas if pure tin is used on these grills, the lead-content of the sardines falls to a negligibly low figure. The metal of the grills, therefore, is the chief source of contamination of sardines with lead. In the authors' opinion the lead-content of canned sardines should not be substantially more than 5 to 8 parts per million; figures above this indicate avoidable contamination during the preparation of the sardines before canning.

"The Chemical Examination of Furs in Relation to Dermatitis. Part II," by H. E. Cox.—Details are given of the kind of fur and mode of dyeing of 216 furs suspected of having caused dermatitis; of these, 37 were undyed, and it is thought that they could not have caused the disease. Chemical tests for the differentiation of *p*-phenylenediamine from Bandrowski's base are given, and also a colorimetric method for determining small quantities of the diamine. Experiments are described showing that *p*-phenylenediamine penetrates the dead skin readily, but does not pass through or into living skin under normal conditions. Some of the reactions of *p*-phenylenediamine with blood and serum are described, and it is shown that it coagulates the proteins and becomes oxidized at their expense; the oxidases present in blood suffice to bring about certain reactions, and if hæmoglobin is present these reactions proceed further. Tyrosine with albumen produces colour reactions similar to those observed with blood. It is suggested that irritation is determined by the abnormal penetration of the diamine through the skin, followed

by its local reaction with certain constituents of the blood or serum yet unknown.

"The Investigation of Japanese Beeswax. III," by H. Ikuta. A new hydroxy fatty acid, $C_{16}H_{32}O_3$, provisionally termed "hydroxypalmitic acid," has been isolated from the mixed fatty acids of Japanese beeswax. It melts at 73·8°–74·2° C., and has a neutralization value of 205·8. It is readily soluble in alcohol, chloroform and ethyl acetate, but is insoluble in cold petroleum spirit and ether. It is sparingly soluble in hot petroleum spirit, and separates in aggregates of white, needle-shaped crystals as the solution cools.

INTERNATIONAL SOCIETY OF LEATHER TRADES CHEMISTS

The biannual Conference of the International Society of Leather Trades Chemists was held at the Colonial Institute, Amsterdam, in conjunction with the biannual meeting of the Internationalen Vereins der Leder Industrie Chemiker. The Conference opened officially on Monday, Sept. 18, the president, Mr. F. C. Thompson, M.Sc., in the chair. After a formal welcome to all present, the meeting proceeded to elect the officers for 1934–35 as follows: *President:* Monsieur C. R. Loos; *Vice-Presidents:* Mr. F. C. Thompson; Monsieur G. Colchin; *Hon. Gen. Sec.:* Dr. J. Gordon Parker; *Hon. Gen. Treasurer:* Prof. D. McCandlish; *Members of Committee:* Dr. C. Schiaparelli, Prof. V. Kubelka, and Dr. P. Chambard.

The hon. general secretary in presenting his report made mention of the publication in book form by the Society of the papers read at the Protein Conference, and the wide sale which this volume had enjoyed. He reported favourably on the financial position of the Society, and stated that the Journal was on a sound financial basis. The balance sheet was read, approved, and adopted.

It was decided to accept the invitation of the Belgian Section to hold the next Conference in Brussels.

In recognition of his international scientific services, Prof. R. Stiasny was unanimously elected an honorary member of the Society.

Mr. F. C. Thompson took for the subject of his Presidential Address "The Measurement of p_H." The importance of p_H measurement was emphasized, and in biological work this factor ranked in importance with temperature. In no industry however was this measurement so important as in that of leather manufacture. The p_H value of every liquor used, from soaks to tan liquors, fat liqnors and neutralizing liquors had to be determined to effect proper control. The speaker then discussed in detail the various methods which had been proposed, mentioning also their limitations for the particular purpose in view. He laid stress on: (1) the need for a careful survey of the methods available for the particular case arising; (2) the need for adequate standardization; (3) the study of the special problems of (*a*) sulphited extracts, (*b*) feebly-buffered solutions, (*c*) salt error of the glass electrode. All these points indicated the need for a commission to deal with the whole question, and he formally proposed the formation of a Commission for the purpose of studying the question discussed, which was seconded by Mr. R. O. Phillips. Receiving the approval of the meeting, Mr. Thompson was elected chairman of this Commission.

On Tuesday, Sept. 19, the joint Conference of the I.S.L.T.C. and I.V.L.I.C. was officially opened by Mr. J. L. Van Gijn, president of the I.V.L.I.C., and also of the Dutch Section of the latter.

Dr. H. R. Kruyt (Professor of Physical Chemistry, Utrecht University) gave a lecture on "The Colloid Chemistry of Collagen and Gelatin." The problem of the nature of collagen, he said, is rendered the more difficult for colloid chemistry as collagen is an insoluble substance, and the soluble cleavage products had to provide us with the insight we wanted. Recent investigations of de Jong on complex coacervation have made us familiar with insoluble substances resulting from two soluble colloids. The theory of coacervation, especially of complex coacervation was developed and collagen shown to be a complex coacervate (with arrangement). The practical aspects of the gelatin and glue industry were treated from this point of view. De Willigen's investigations on the complex coacervation of gelatin and chondroic acid and mucoitin demonstrated the possibility of complex coacervation with animal colloids. Lack of knowledge of the real complex builders was discussed together with conclusions from this working hypothesis regarding histology, embryology, and the tanning processes. At the close of the lecture there was a lengthy discussion in which Dr. Gustavson, Prof. Bergmann, Dr. Dorothy Jordan Lloyd, and others took part.

On Wednesday, Sept. 20, the Conference opened with a joint meeting of the two societies, and the Leather Analysis Commission report was presented by Drs. Jablonski and Chambard.

Dr. Jablonski reported that no further work had been done on chrome leather analysis, but that during the next two years Mr. Innes will be studying the matter more fully. A short report on the physical properties of leather was also given by Dr. Jablonski, after which there was a joint meeting with the International Tanners Council, with Mr. Van Gijn in the chair. An interesting film was then shown on the warble fly. The life cycle of the fly was illustrated, also damage caused through infected animals rubbing themselves against barbed-wire fencing. The Government strongly recommended farmers not to use barbed wire.

Prof. M. Bergmann followed with a lecture on hides and skins, and after a discussion it was agreed to form a committee to consider the question of hide and skin improvement, especially in connexion with warble damage. This committee consists of W. Freudenberg and Dr. E. Snow (representing tanners) and Prof. M. Bergmann and Dr. A. Gansser (representing chemists).

Wednesday afternoon and Thursday were occupied by the reading of the following papers:

"The Prevention of Deterioration of Vegetable Tanned Leathers," by D. McCandlish and W. R. Atkin. An explanation of the greater fixation of sulphuric acid from polluted atmospheres by catechol tanned leathers as compared with pyrogallol leathers is offered. This is due to an oxidation-reduction cycle in which the catechol tannin acts as a catalyst in the production of sulphuric

...d from the sulphur dioxide in the atmosphere. To ...vent acid adsorption, it is proposed to give leather negative Procter-Searle value by incorporation of ...itable salts of weak acids.

The Influence of the Pre-Chroming of Hide upon its ...xation of Vegetable Tannins," by K. H. Gustavson. ...getable tannins are fixed at a greater rate by pre-...hromed hide than by pelt at the same experimental ...nditions. The maximum tannin fixation by chromed ...ock is obtained upon 2 to 3 months' duration of tanning, ...here as this limiting value of tannin fixation by pelt is ...ached first after several years of tanning. For practical ...urposes it follows that a pre-chroming of hide leads ...ot only to a higher rate, but also to a greater capacity ...f tannin fixation by chromed hide than by untreated ...elt. An explanation of these findings is attempted ...n the basis of the "zwitter-ion" theory of protein ...onstitution.

"The Glass Electrode and Sulphated Oils," by D. Burton and G. F. Robertshaw. The importance of the ...H is shown by the following: (1) *Manufacture*. The ...H is adjusted according to the purpose for which the oil ...s intended and is generally between 6·0 and 8·5 in ...olutions of commercial oils containing 1 g. in 250 c.c. ...ater. (2) *Use*. (a) It is often thought that sulphated ...ils for oiling off and fat-liquoring are satisfactory if ...hey have a p_H of about 7·0 but this is frequently not so. ...he desirable p_H depends upon the acid figure (p_H) of ...he vegetable or chrome leather. If the emulsion of the ...il is not stable at the acid figure (p_H) of the leather oil ...marks may be formed on the surface. (b) The p_H of the ...il must be determined at the concentration at which ...t is to be used and therefore the effect of dilution ...s important. (c) The p_H is not always the same at 20° C. ...s at 50° C. as given by the colorimetric method. This ...oint is being investigated. (d) The buffer index gives ...nformation of practical value. (e) Poor quality oils, ...which decompose on standing, can be detected because ...he p_H falls. (3) *Composition*. Much information about ...he COOH, OSO_2OH and SO_3H groups can be obtained ...by titration curves.

"Oxidation of Fish Oils by Means of Chromic Acid and Bichromates in the Presence of Acid" by A. Dohogne and G. Rezabek. Oil tannage is at present considered ...o be the result of oxidation at the double bonds of the ...il molecule, with the production of peroxides. These ...atter combine with the hide substance to form leather. ...hambard has studied the catalytic action of metallic ...esinates on oil tanning, while the present authors are ...nvestigating the action of chromic acid on this par-...ticular tannage. The first part of the work deals with ...he oxidation of cod-liver oil by aqueous chromic acid ...s a function of time and concentration of chromic ...acid. Contact between oil and the aqueous solution is ...avoured by agitation.

"Action of Anti-Oxidants on the Oxidation of Var-...nishes," by Dr. F. Baldracco. Linseed oil is frequently ...employed in the manufacture of patent leather. During ...he ageing process the film of oil undergoes a high degree ...of oxidation, and it is therefore possible to regulate ...he oxidation, accelerating it by the addition of oxygen ...carriers (driers), or retarding it by means of anti-oxidants. In this paper the author has studied (1) the effect of ...ozone, (2) the effect of sunlight, and (3) the effect of ultra-violet light on pure linseed oil; also on a mixture of linseed oil with anti-oxidants such as stearic and various other commercial products possessing similar properties. He has found that the addition of these products has a very marked action in retarding oxidation. This retardation is very marked during the early stages of drying.

"Further Notes on the Wearing Resistance of Sole Leather," by J. Gordon Parker.—The practical value of the Thuau machine has been thoroughly tested. From a hide which has been tanned in pits, a regular curve is produced, but where the process is accelerated by drumming or other similar methods, this in most cases is clearly shown by a break in the curve. The results obtained have been found to be of great value in controlling experimental work in the tanyard.

"Analysis of Raw Hide," by Dr. E. Simoncini.—Raw hide is seldom submitted to chemical analysis in order to ascertain the mode of preservation or its actual value, while very little is published in the literature on the exact chemical composition of either hides or skins, and no specific standard appears to be laid down. The weight of the hide or skin is not sufficient for control. It is necessary to know the moisture content, proportion of salt in relationship to the hide weight, and the proportion of salt to protein matter. Methods of analysis need carefully standardizing. For sampling raw hide the author proposes to use the present method of sampling as laid down by the I.S.L.T.C. He also details the methods for the determination of moisture, soluble nitrogen, hide substance, etc.

"Combination of Colouring Matter with Collagen (Part II)," by Dr. G. A. Bravo and Dr. F. Baldracco.—Continuing their investigations into the combination of colouring matters with purified hide powder, the authors have studied the power of combination of acid and basic dyes. It was shown by the authors in their first communication that acid dyestuffs combine with hide powder both by chemical combination and by physical adsorption, in accordance with the well-known adsorption formula, and the swelling of proteins as established by Procter and Wilson; but with basic dyestuffs the action is not the same.

"Direct Use of Hide Powder for Detannization," by Dr. A. Jamet.—Attempts have been made to simplify tannin analysis by the direct use of hide powder for detannization. Based on the work of Willstätter, a proposal is made for the removal of the soluble matter in the hide powder by adsorption with an excess of kaolin. The adsorptive power of the kaolin was tested against gelatin solution and a solution of the soluble matter from F.1 hide powder, and in both cases adsorption was to the extent of 95%.

"Gelatin-Tannin Reaction," by F. C. Thompson.—The studies of J. T. Wood and J. v. Schroeder support the contention that the reaction should not be described as an example of adsorption. In the light of this and more recent work, it is probably best to consider the reaction as the production of an insoluble, non-ionized compound by means of ordinary chemical forces. There is quantitative evidence to show that gelatin combines with tannin in the same way as with hydrochloric acid.

CORRESPONDENCE

CHEMICAL STONEWARE

SIR,—I have read with great interest the letter on Chemical Stoneware in your issue of September 29.

I was present at the discussion on lead-lined plant and chemical stoneware to which your article of September 22 referred. If Mr. Barrett would read that article again he would find that the definite claim of withstanding a temperature of 220° C. is made for British stoneware. This is certainly not "vague."

I agree with him that the choice of words referring to the glaze on stoneware being frequently more porous than the body, is unhappy; but this is mere quibbling. Mr. Barrett knows, as well as I know, that it is impossible commercially to produce a glaze which, in its extremely thin layer, will not have a flaw or pinhole through which the body will be attacked. Quality of body is more important in stoneware than that of the glaze.

Mr. Barrett's notes on iron in glazes are excellent and for general purposes I agree that the presence of iron is not objectionable. For certain work there is no doubt that the glaze is definitely attacked, and in such cases its iron content becomes important.

With regard to the porosity of stoneware I would suggest that Mr. Barrett makes himself acquainted with recent developments both on the Continent and in this country if he doubts whether the supply of large pieces of chemical stoneware plant with 1% porosity is possible of attainment.

I am, Sir, etc.,

G. N. HODSON

Loughborough

Oct. 4, 1933

CHEMISTRY AND AGRICULTURE

SIR,—In the concluding part of Dr. Alexander Lauder's article on "Chemistry and Agriculture" he attributes to calciferol (crystalline vitamin-*D*) the formula $C_{27}H_{42}O$. Calciferol is certainly an isomer of ergosterol, of which it is an irradiation product: it must, therefore, have the formula $C_{28}H_{44}O$, since this has now been generally accepted as the empirical formula of anhydrous ergosterol.

I am, Sir, etc.,

A. L. BACHARACH

London, N.W.1

Oct. 6, 1933

METRIC UNITS OF VOLUME

SIR,—The decision of the B.S.I. to use the millilitre as a unit of *volume* is about as logical as it would be to define the capacity of a gasholder in gallons, or the volume of an iron casting in drachms. If the unit of length is the metre, the unit of volume must surely be the cubic metre, of which the cubic centimetre is the natural derivative.

As such, it has no reference to a certain weight of water, as "Anon" infers.

In view of the fact that for all practical purposes equivalence of c.c. and ml. may be assumed, there appears to be no need for a separate system of units for capacity as distinct from volume, and it would be more logical to re-define the volume of a litre as 1000 c.c. exactly, in which case the need for the precise definition of the temperature, pressure, purity, etc. of the water would be obviated. Particularly is this desirable in view of your report of the production of a small amount of water having a density over 1·01. Does this mean that the definition of the millilitre must be dependent upon the concentration of H^2H^2O in the water?

Apart from strict definition, however, considerations of euphony should exclude such a tongue-twister as "millilitre."

As predicted by "Anon" therefore, I shall continue deliberately to say and to write "c.c.," but when doing so, I shall not really mean "ml." as he infers.

I am, Sir, etc.,

F. E. MILLS

Brentford,

Middlesex

Oct. 9, 1933

PERSONAL AND OTHER ITEMS

We regret to announce the death of Mr. A. E. Johnson, borough analyst of Wolverhampton, and for many years a member of the Society. He took up his post at Wolverhampton in 1922, and held similar appointments at Stoke-on-Trent and Newcastle-under-Lyme.

We regret to learn of the death on October 2 of Prof. J. E. Marr, emeritus professor of geology at Cambridge. Prof. Marr was elected a Fellow of the Royal Society in 1891, and was awarded a Royal Society Medal in 1930. He was president of the Geological Society of London from 1904 to 1906.

Dr. H. J. Rose, a senior fellow of Mellon Institute of Industrial Research, Pittsburgh, has been elected chairman of the Gas and Fuel Division of the American Chemical Society for the year 1933—34. Dr. Rose has made many important contributions to the literature of by-product coke technology and coal classification; he is now head of a multiple industrial fellowship that is engaged in research on anthracite.

Mr. K. S. Murray has signified his intention of resigning from the positions of chairman and managing director of British Oxygen Co., Ltd. at the end of this year. Subject to the approval of shareholders he has been appointed an honorary governor of the company for life, and has accepted the position of consulting engineer of the company. Mr. Murray was associated with the company's first successful operation of the barium process for isolating atmospheric oxygen.

Prof. H. E. Simmons, head of the chemistry department of Akron University, Ohio, has been appointed president of the University. Prof. Simmons has been associated with the chemistry department for 23 years and has been largely responsible for the courses in rubber chemistry which have made the University well known.

Dr. Erwin Schrödinger, who was formerly professor of theoretical physics at the Friedrich Wilhelm University, Berlin, has been appointed to a Supernumerary Fellowship at Magdalen College, Oxford.

We regret to learn of the death on October 7 of Mr. J. Davison, general manager and a director of Barrow Hæmatite Steel Co. Mr. Davison was a member of

National Committee which was set up last year to ...der the reorganization of the iron and steel industry.

...e regret to learn of the death in Calcutta of Mr. ...I. Hughes, chairman of Imperial Chemical Industries ...ia), Ltd.

...he Weston Fellowship for 1933—34 of the Electro...mical Society of America has been awarded to ...R. D. Blue, who is working at Indiana University ...he electrodeposition of aluminium.

...r. I. W. Wark has been awarded the Syme prize of ...University of Melbourne, consisting of a bronze ...al and £125, for his research work in recent years ...metallic complexes with hydroxy-acids, certain ...ets of thermodynamics, and the electrodeposition ...inc.

...rof. C. W. Oséen, professor of physics in the University ...psala has been appointed head of the Institute of ...sics of the Nobel Foundation, near Stockholm.

...further grant of probate has been issued in respect ...ttled land valued at £5460 in the estate of the late ...Richard Threlfall, G.B.E., F.R.S., who died in ... 1932, leaving unsettled estate already valued at ...133.

...r. E. G. Cubitt, agriculturist and director of Lawes ...mical Manure Co., left estate of gross value £40,518, ... net personalty £2070.

...ajor G. M. Palmer, chairman of the Manley Hill ...mical Company and the Chislet Colliery, left estate ...he gross value £49,796, with net personalty £41,901.

...lee of Bradford Technical College

...n Saturday, Oct. 7, the Bradford Technical College ...rated its Jubilee, the College having been established ...une, 1882. The Rt. Hon. The Earl of Athlone, K.G., ...ncellor of London University, opened a new wing of ...College and unveiled a Tablet commemorating the ...sion. There was present a large assembly of students ...resent and past—and invited guests, which included ...J. A. Craven, vice-chairman, and Mr. H. J. Hodsman, ...etary, of the Yorkshire Section of the Society of ...mical Industry.

...rican Sulphuric Acid Patent

...he U.S. Circuit Court of Appeals, Third Circuit, ... dismissed the appeal of the General Chemical Co. ... action concerns patent No. 1,371,004, granted in ... to Slama & Wolf, containing a claim for the use ...anadium and kieselguhr as catalyst. The court ... that there was insufficient disclosure of the alleged ...ntion and there was no infringement of the patent.

...rochemical Society of America

...he Electrochemical Society, Inc. of America has ...ded to make its Spring Meeting in 1934 a joint ...ting with the American Ceramic Society. The ...ting will be held at Asheville, North Carolina, and ...two main sessions will be concerned with discussions ..." The Relation of Chemical and Physical Structure ...ielectric Behaviour" and "Refractories."

...emical Distributors' Organization in U.S.A.

...iscussions have been proceeding in America with the ...ct of forming an Institute of Chemical Distributors, ...mbrace all those concerned with the marketing of chemicals and allied products. An organization committee, composed of the representatives of many famous concerns, has been at work and has adopted a constitution for the proposed organization.

Improvement in the Artificial Silk Industry

A general improvement has taken place during the last six months, according to figures published in *Die Chemische Fabrik*. Production in the United States for the first half of 1933 was 31·72 million kg., compared with 22·77 million kg. for the same period in 1932. Other figures are: Japan 18·335 (12·865), Germany 17·09 (12·115), France 10·86 (8·765), Holland 5·32 (3·77) million kg. English production for the first half of this year is reported as 37·01 million lb., which is 2·55 million lb. above the figure for the second half of 1932.

Starch Manufacture in India

Starch is used in considerable quantities in India and some 25,000 tons are imported every year. The Department of Industries of the Bombay Provincial Government, working with the Royal College of Science, Bombay, has recently shown the cereal Jowar to be an ideal basis for starch manufacture, and a suitable process of extraction has been developed. Textile mills have reported very favourably on the product.

New Ammonium Sulphate Plant in Norway

It is reported that the Norsk Hydro-Elektrisk Kvaelstofaktielskab, the well-known Norwegian concern manufacturing nitrates, is to construct a plant at Heren for the production of sulphate of ammonia, a product which it has not previously made. The plant is expected to be complete in about a year. The company has recently completed the erection of a soda-ash plant with a capacity of 18,000 tons a year.

French Bauxite and Aluminium Industry

In the last two years the production of bauxite in France shows a considerable decrease. In 1932 it was 350,000 tons, in 1931 380,000 t., in 1930 609,200 t., and in 1929 666,400 t. The export of bauxite, on the other hand, was 212,487 t. in 1932, compared with 167,837 t. for 1931. 24,640 t. of aluminium were produced in 1930, but the figure dropped to under 20,000 t. in 1931. The export of aluminium is small, but also shows a decline (838 t. in 1932; 3066 t. in 1930).

New Chilean Potash Deposits

Extensive deposits of potassium chloride are reported to have been discovered in the neighbourhood of Antofagasta, Chile. The area measures 25 km. by 75 km., but if it is to be developed, a new railroad of 100 kilometres will be necessary for transport.

Increased Japanese Production of Formic and Oxalic Acids

The Yedogawa Works in Yokohama has increased its production of formic acid from 50 tons to 150 t. a month. At present the monthly export is 20 t. This is taken principally by the Dutch Indies. A similar development in the manufacture of oxalic acid is projected. (*Die Chemische Industrie.*)

Gold and Silver in India

A note in *The Times* states that according to Mr. V. Sondhi of the Geological Survey of India, a survey of the southern Shan States has revealed the presence of

gold, silver, and lead in quantities sufficient to warrant exploitation if conducted on a sufficiently big scale.

Trade Improvement in Germany

The production of leather in Germany is reported as being 20% greater than for the corresponding period last year (*Die Chemische Industrie*). A sharp rise in the output of the textile industry in recent months has brought production back to the 1931 level, while in the cotton-spinning industry figures are approaching those for 1927. This expansion appears to be due to developments in the home market.

A Pigment and Colour Index

The Educational Bureau of the American Paint and and Varnish Manufacturers' Association, Washington, has issued a booklet called "Pigment and Colour Index for 1933" that contains a large amount of up-to-date information. It follows previous publications on the same lines now out of print, and ten or more workers have been engaged for some months in getting the numerous details together. More than 1200 white and coloured pigments have been dealt with, and a large number of firms have provided information regarding their products. The commercial name of each pigment is given first, followed by the name of the maker. In the next column information voluntarily submitted by the maker is given; the number of cases where no such information is given is relatively small, and in many cases accurate analytical details are provided. Other columns give specific gravities, weights per gallon, bulking values, fineness residues on 325-mesh screen, and oil absorption.

Atmospheric Pollution

A plan for a community campaign against air pollution in cities has been put forward by H. B. Meller, of the Mellon Institute of Industrial Research, Pittsburgh, in an article, copies of which can be obtained from the Institute. The article reviews the failure of efforts toward smoke abatement in the past, and suggests that much good could be done by stricter regulations. These regulations should insist (1) on selection from the large number of makes of boilers, furnaces, automatic feeds, etc. to eliminate *dense* smoke; (2) alterations and repairs of plant to achieve the same degree of smokelessness; (3) the use of dust separators; and be so framed as to take advantage of advances toward smokeless and dustless fuels.

The plan of campaign suggested is to divide the "smoke area" into districts, which should then be used to make a survey of air pollution, viz., the "soot-fall," air-borne solids, and sulphur dioxide in the atmosphere of each. A survey should then be directed to determine the efficiency and cleanliness of fuel-burning equipment in each area, and ultimately legislation should be enacted in the light of knowledge gained in the surveys to ensure measures being taken to reduce the extent of pollution.

British Colour Council

During the past eighteen months the British Colour Council has been working intensively on the preparation of a British Colour Council Standard Card, and the card is shortly to be issued. The production of the card will mark a notable achievement in colour definiti Patterns of pure silk ribbon with a name allotted to ea will make known as standards those colours which a used in all industries and for which there is a permane demand. In the past various samples of colour ha borne the same name, whilst a single colour may ha been known by several different names. It has al been necessary to study foreign translations, as t equivalent words in two languages do not alwa describe the same colour. A dictionary is to be issu with the card, and will give information respecti the 200 odd colours in the card, with names by whi they were previously known, and foreign names. T standardization of certain colours will not affect t production of "exclusive" colours by any firm, or t seasonal fashion colours promoted by the British Col Council.

COMPANY NEWS

BORAX CONSOLIDATED, LTD.

The company has announced the payment November 1 of the half-yearly dividend on the 5½% cumulative preference shares. This announceme follows the statement made early this year that co sideration of a dividend would be postponed until t accounts for the financial year ended September 30 we available.

BABCOCK & WILCOX, LTD.

The directors of the company have declared interim dividend of 3% less tax, as against 4½% la year, when the final dividend was 3%. The inter dividend is payable on the £4,299,656 ordinary capit

BURT, BOULTON & HAYWOOD, LTD.

Net profit of the company for the year ended June was £10,500, as compared with £45,800 last year, a dividend on ordinary shares is recommended at 3½ as previously announced, against 8% last year. T balance sheet shows total investments of £387,703 subsidiary and other companies, and working capital joint trading concerns is £120,188.

STANTON IRONWORKS CO., LTD.

The announcement recently of the formation of new company named Cochranes (Middlesbrough), L indicates that the control of Cochrane & Co. of Middl brough has now passed to Stanton Ironworks, Lt which was reported previously to have acquired t company from the Cargo Fleet Iron Co., Ltd. Cochra & Co. are well-known manufacturers of pipes and tub It is stated that the Middlesbrough works will alm certainly be maintained and developed.

IMPERIAL SMELTING CORPORATION, LTD.

An agreement has been reached with the Sulphi Corporation, Ltd., whereby a subsidiary of the Imper Smelting Corporation, Ltd. will acquire the spelt zinc oxide, and sulphuric acid works of the Sulphi Corporation at Seaton Carew, near West Hartlepo The Imperial Smelting Corporation has also arrang to acquire the share capital of the Delaville Spelter C of Birmingham. The purchases do not involve t raising of any fresh capital.

MARKET REPORT

This Market Report is compiled from special information received from the manufacturers concerned.

Unless otherwise stated, the prices quoted below cover bulk quantities net and naked at sellers' works.

The following alterations in prices are reported since the publication of the last Market Report (cf. Chem. & Ind., Oct. 6, 1933, p. 802).

TAR PRODUCTS

Acid Cresylic, 99/100.—1s. 6d.—1s. 9d. per gal. Refined, 1s. 8d.—1s. 9d. per gal. Pale, 98%, 1s. 4d.—1s. 5d. per gal. 95%, 11d.—11½d. per gal. Dark, 10d. per gal.

Creosote.—B.S.I. specification, 3d.—3½d. per gal., d/d. *Heavy*—4d. per gal.

Naphthalene.—Purified crystals, £9 15s. per ton in bags. Crude, Hot Pressed, £6 5s. per ton.

Pitch medium, soft.—77s. 6d.—80s. per ton, in bulk at makers' works.

Toluole.—90%, 2s. 4d.—2s. 5d. per gal. Pure, 2s. 9d.—2s. 10d. per gal.

Xylol.—2s. 4d.—2s. 5d. per gal. Pure, 2s. 5d.—2s. 6d.

PATENT LIST

The following is a list of complete specifications of chemical interest which are open for inspection under Section 91 (4) (*a*) of the Patent Acts. Printed copies are not available, but photographic copies may be obtained at a charge of 8d. per page (minimum 1s.) from the Patent Office, Chancery Lane, W.C.2

I. 3349 (1933). Houdry Process Corp. Catalytic materials.

8869—73 (1933). Glasplakatefabr. Union. Viscosimeters.

II. 36,749 (1932). Standard Oil Development Co. Lubricating oils.

8420 (1933). Comp. Gén. de Distillation et Cokéfaction à Basse Temp. Low-temperature carbonization retort ovens.

III. 5676 (1933). Röhm & Haas Co. Preparing alkylated phenols.

7237 (1933). *Riedel–de Haën A.-G.* Making the monoalkyl ethers of protocatechnic aldehyde.

7422 (1933). I. G. Farbenind. Manufacture of nitrogenous condensation products.

8702 (1933). I. G. Farbenind. Manufacture of halogenated ethanols.

8811 (1933). Röhm & Haas A.-G. Manufacture of polymerization products of acrylic acid or its homologues or derivatives.

8953 (1933). I. G. Farbenind. Manufacture of 4-amino-1:8-naphthalenedicarboxylic acid amide and derivatives.

IV. 8848 (1933). *Gaspar.* See XXI.

V. 8538 (1933). Brit. Thomson-Houston Co. Coating bodies with fibrous material.

9002 (1933). Sindl. Producing cellulose esters.

9003 (1933). Sindl. Stabilizing organic esters of cellulose.

9056 (1933). *Du Pont Viscoloid Co.* Manufacture of cellulose nitrate.

VII. 6414 (1933). Mathieson Alkali Works. Manufacture of ammonium chloride and sodium carbamate.

8680—2 (1933). I. G. Farbenind. Production of dilute acids.

X. 2654 (1933). Soc. des Aciéries de Longwy. Improving iron or steel.

XI. 5233 (1933). Westinghouse Electric & Manuf. Co. Cathodes.

6660—1 (1933). Fery. Accumulators.

8642 (1933). Hartel. Gettering electric discharge valves.

XIII. 8578 (1933). *Du Pont de Nemours & Co.* Manufacture of synthetic resinous compositions.

8811 (1933). Röhm & Haas A.-G. *See* III.

8970 (1933). Krebs Pigment & Color Corp. Manufacture of pigments.

XIV. 8295 (1933). Goodyear Tire & Rubber Co. Preserving rubber.

8526 (1933). Laurin and Bidot. Rubber substitute.

XXI. 8847 (1933). Gaspar. Recording materials for colour films.

8848 (1933). Gaspar. Photographic material for producing dyestuff images.

8849 (1933). *Gaspar.* *Photographic material for the* production of hydrotype images.

XXII. 9056 (1933). Du Pont Viscoloid Co. *See* V.

GENERAL NOTES

Official Trade Intelligence

The Department of Overseas Trade (Development and Intelligence), 35, Old Queen Street, London, S.W.1, has received the following inquiries for British goods. British firms may obtain further information by applying to the Department and stating the specific number. *Australia:* Packings—Petrol- and oil-resisting, in sheet form (372). *British India:* Wood preservatives (Order No. M-3533: B.Y. 7676). *British Malaya:* Hardware, paint and varnish (374). *Canada:* Salt cake, slab alum, barytes, China clay (379): Paper-making machinery and plant (380). *Egypt:* Aluminium and copper, iron and steel, soap (394). *Finland:* Red earth, zinc white, etc. (392). *Palestine:* Acid oils and dyes (383). *South Africa:* Steam-raising plant (pump, economizers, draught plant, steam piping) (G.Y. 13,028).

Dyestuffs (Import Regulation) Act, 1920

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during September has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee. The total number of applications received during the month was 657, of which 543 were from merchants or importers. To these should be added the 6 cases outstanding on August 31, making a total for the month of 663. These were dealt with as follows: Granted 646 (of which 642 were dealt with within 7 days of receipt); referred to British makers of similar products 9 (all dealt with within 7 days of receipt); outstanding on September 30, 8. Of the total of 663 applications received, 651 or 98% were dealt with within 7 days of receipt.

Tellurium Lead

The "Teledium" brand of Tellurium lead contains less than 0·1% of tellurium, and this small percentage confers on lead a fine-grain structure, work-toughening properties, and a greater resistance to corrosion. A pamphlet describing its properties and uses has been prepared by Goodlass Wall & Lead Industries, Ltd. of London House, New London Street, E.C.3, and may be obtained on application to them.

A New Solochrome Dye

Imperial Chemical Industries, Ltd. has recently added Solochrome Cyanine RS to its range of dyestuffs. It is of interest on account of the brilliancy of its shade and its excellent fastness to milling, potting, etc.; it will be used also for brightening navy blues fast to milling and for replacing acid violets as the blue components of mode shades where brightness and fastness to milling are desired. Its good fastness to "acid planking" makes it suitable for dyeing loose fur used in hat manufacture. Good dischargeability also permits of its use in discharge or resist styles. It possesses good affinity for the wool fibre, and may be applied to natural silk by either the afterchrome or chromium chloride mordant process.

Kingston's Metric Equivalent Tables

Kingston's Translations Institute of 101, Leadenhall Street, E.C. has published (price 1s. 1d.) a convenient card of tables for converting metric measurements into English ones. If you wish to know the weight in pounds of 100 cu. in. of water you can find it out by this table, by suitable calculation. If our calculation is correct 100 cu. in. of water are about 0·36 gal. and weigh about 3·6 lb.

A New Automatic Still

Baird & Tatlock, Ltd., the well-known manufacturer of scientific apparatus, of Cross Street, Hatton Garden, London, E.C.1, has recently placed on the market a new electrically heated automatic still which should be of particular interest to laboratory workers and others who have a constant demand for distilled water. The body of the still is of copper, heavily tinned inside. A safety device is incorporated which automatically ejects the electric plug, cutting off the current, if the water supply fails or is inadvertently cut off. Operation is entirely automatic, and with a consumption of 1500 watts the output is 4 pts. per hour, or with 2000 watts, 5½ pts. per hour, the cost being put at less than 3d. per gal. The still can be supplied in forms suitable for wall-fixing, shelf fixing, or with a stand for screwing to the floor.

Automatic Control in Steel and Gas Works

Automatic control equipment is a necessity in steel and gas works for the satisfactory working of plant. Those concerned with such control will find a leaflet issued by James Gordon & Co., Ltd., Regent House, Kingsway, London, W.C.2, of interest. This leaflet describes briefly some of the applications of Hagan automatic regulators for the control of pressure, flow, mixing of gases, ratio between air and gas, draught, and temperature.

A difficulty with automatic operation in some of the steel and gas works processes, which has had to be overcome, results from the intermittent nature of the processes, requiring different operating conditions as the processes advance. This difficulty has been removed by the flexibility and ease of adjustment of Hagan regulators which, if required, can be adjusted from a central control point. Hagan regulators can therefore be used to advantage for intermittent processes in addition to those which are continuous.

Patents and Trade Marks

A little book entitled "Patents and Trade Marks" has recently been re-issued by King's Patent Agency, Ltd., of 146A, Queen Victoria Street, London, E.C.4, and it will be found a very useful guide to terminology and procedure in what is often a perplexing subject. With the changes that have taken place in recent years it is as well to have in concise form a guide to existing practice. The book can be obtained, post free, on application to King's Patent Agency, Ltd.

Thermostatic Switches

The Drayton Regulator & Instrument Co., Ltd., of West Drayton, Middlesex, are now producing the "Eost" thermostatic switch in a new form. The overall dimensions of the base have been considerably reduced, the mechanism has been modified to reduce friction to a minimum, and the porcelain terminal block has been made accessible without removal of the main cover. These switches are available for temperatures up to 900° C.

A leaflet (List No. 161A), giving full particulars of this type of switch, can be obtained from the company.

PUBLICATIONS RECEIVED

HYDROGEN PEROXIDE BLEACHING OF WOOL, COTTON, AND SILK. By I. E. Weber, B.Sc. Paper read at the *Textile Institute Annual Conference at Harrogate*, June, 1933. Pp. 16. Luton: B. Laporte, Ltd., 1933.

GMELIN'S HANDBUCH DER ANORGANISCHEN CHEMIE. 8th new revised edition. Edited by the German Chemical Society. Revised by R. J. Meyer. System-Number 54. Wolfram. Berlin: Verlag Chemie, G.m.b.H., 1933. 64 m. Subscription, 56 m.

REPORT ON THE WORK OF THE MINING RESEARCH LABORATORY OF THE UNIVERSITY OF BIRMINGHAM DURING THE YEAR 1932. Executive Board of Mining Research. Pp. 17. Birmingham: D. McMichael, 1933.

GOLD IN CANADA, 1933. By A. H. A. Robinson. Canada Department of Mines. Mines Branch. No. 734. Pp. vii + 92. Ottawa: J. O. Patenaude, Acting King's Printer, 1933. 20 c.

REPORT OF H.M. ELECTRICAL INSPECTOR OF MINES FOR THE YEAR 1932. Mines Department. Pp. xiv + 64. London: H.M. Stationery Office, 1933. 1s.

A MANUAL OF PRACTICAL INORGANIC CHEMISTRY: QUALITATIVE ANALYSIS AND INORGANIC PREPARATIONS. By Dr. E. H. Riesenfeld. Translated by P. Rây, M.A. Pp. xxiii + 471. Calcutta: Chuckervertty, Chatterjee & Co., 1933. Rs. 6; 9s.

BENTLEY AND DRIVER'S TEXT-BOOK OF PHARMACEUTICAL CHEMISTRY. Revised by J. E. Driver, Ph.D., M.Sc. 2nd ed. Pp. xiv + 538. London: H. Milford, Oxford University Press, 1933. 16s.

SPARKS FROM THE ELECTRODE. By C. L. Mantell, Ph.D. A Century of Progress Series. Pp. x + 127. Baltimore: Williams & Wilkins Co.; London: Baillière Tindall & Cox, 1933. 5s.

DAS SYSTEM KIESELERDE QUARZGUT UND QUARZGLAS SILIKASTEINE. By Dr. E. Zschimmer. Pp. viii + 138. Stuttgart: F. Enke, 1933. 13 rm.

DETECTION AND DETERMINATION OF SMALL AMOUNTS OF INORGANIC SUBSTANCES BY COLORIMETRIC METHODS. By N. Strafford, M.Sc., F.I.C. Pp. 36. Reprinted from *the Journal of The Institute of Chemistry of Great Britain and Ireland*, 1933.